(12)

EUROPEAN PATENT APPLICATION

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2 Date of filing: 01.03.88

A request for correction of page 1 of the originally filed description has been filed pursuant to Rule 88 EPC. A decision on the request will be taken during the proceedings before the Examining Division (Guidelines for Examination in the EPO, A-V, 2.2).

The title of the invention has been amended (Guidelines for Examination in the EPO, A-III, 7.3).

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- Designated Contracting States:

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- Broad spectrum antimicrobial system for a hard surface cleaner.
- (F) A liquid hard surface cleaner having broad spectrum disinfectancy activity based on a synergistic effect between pine oil and organic, oil soluble acids at a pH of 0 to 6. The cleaner has disinfectancy activity against both gram positive and gram negative organisms.

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NOVEL BROAD SPECTRUM ANTIMICROBIAL SYSTEM FOR HARD SURFACE CLEANERS

This invention relates to a liquid hard surface cleaner having broad spectrum disinfectancy and containing pine oil.

A number of pine oil containing cleaners are known for cleaning hard surfaces, i.e. porcelain, enamel, plastic laminates and the like. Such cleaners are effective for cleaning greasy soil, and in combination with certain surfactants they have been effective in cleaning grimy soil from surface. However, pine oil based cleaners have not been found to have broad spectrum antimicrobial activity since they are only effective against gram negative organisms and not against gram positive organisms unless quaternary ammonium compounds are present. The use of quaternary compounds in a cleaner is not desirable since these compounds have a number of undesirable qualities. A high residue is left on the surface after cleaning. In addition, quaternary ammonium compounds are too toxic for this use and are highly irritating to the skin, eyes etc.

It is therefore an object of this invention to provide a pine oil containing hard surface cleaner that has broad spectrum disinfectancy, but does not contain quaternary ammonium compounds.

It is now been found that the above object may be attained by the use of certain organic oil benzilic acid, salicylic acid and phthalic acid; organic straight chain carboxylic or hydroxy carboxylic acids such as sorbic acid, malic acid, malonic acid, glutaric acid, adipic acid, tartaric acid and citric acid and nitrogen containg heterocyclic acids such as picolinic and nicotinic acids. Such acids are well known and widely used, but to our knowledge have not been used as a component of a disinfectant cleaning composition.

The ingredients and amounts that make up the hard surface cleaner of the present invention are listed in Table I below. It will be understood that the listing of oil soluble organic acids and of detergents is exemplary and not inclusive.

TABLE I

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CONCENTRATION RANGES OF RAW MATERIAL

30	CONCENTRATION	ACTIVE INGREDIENTS
35	1.00 to 30.00 0.05 to 5.00	Pine Oil Oil soluble acid: Sorbic, Benzoic Salicylic, Phthallic, Benzilic
40	CONCENTRATION	INERT INGREDIENTS
45	0.10 TO 10.00 0.01 to 2.00 0.01 to 1.00 0.01 to 2.00	Isopropyl Alcohol Fenchyl Alcohol Ammonium Hydroxide Ethylene diamene tetra acetic acid.

Optionally one or more of the ingredients listed below for effective detergency.

	q.s	Water
15	0.10 to 10.00	Sodium Pareth-25 Sulfate
	0.10 to 10.00	Sodium Cl4-Cl6 Olefin Sulfonate
10	0.10 to 10.00	Polyoxyethylene (8) C9-C11 Ether
5	0.10 to 10.00	Sodium Dodecyl Benzene Sulfonate
·	0.10 to 10.00	Sodium Cl3-Cl8 Paraffin Sulfonate
		· · ·

100.00%

As previously described, pine oil is not effective against gram positive organisms, although it is effective against gram negative organisms. It is, therefore, surprising that a combination of pine oil and an oil soluble organic acid, as described previously, has broad spectrum disinfectancy and is effective against both gram negative and gram positive bacteria at a pH of 0 to 6. We have found that this is a truly synergistic effect since a composition containing pine oil but no oil soluble acids was ineffective against Staphylococcus aureus (gram positive). A similar composition containing pine oil but no oil soluble acids was also ineffective against S. aureus. However, a similar composition containing both pine oil and oil soluble organic acids at a pH of 0 to 6 was surprisingly found to be 100 per cent effective against S. aureus. Thus, this composition has broad spectrum disinfectancy since it is effective against both gram positive and gram negative organisms.

The present liquid hard surface cleaner thus has use in hospitals, due to its broad spectrum activity, in industrial use and consumer use. The active ingredients were effective on bacteria grown on either nutrient broth or synthetic media. The composition, according to the invention, gives excellent cleaning on greasy, 35 grimy, fingerprint and soap scum soils. The combination of pine oil and oil soluble organic acids is safe

enough for use as a consumer product.

In order to demonstrate the synergistic broad spectrum disinfectancy effect of the cleaner of the present invention, the following specific Examples are set forth:

Example I to III

A formulation (I) according to the present application was prepared with the ingredients and amounts thereof as shown in Table I and having a pH of between 0 and 6.

A second formulation (II) was prepared identical to formulation I, except that the oil soluble acid was not included.

A third formulation (III) was prepared identical to formulation I, except that the pine oil was not included.

Example II

Formulations of II and III of Example I were subjected to microbiological testing according to the Association of Official Analytical Chemists - Use Dilution Method (AOAC-UDM) procedure as used by the Environmental Protective Agency (EPA) and industry in general, against S. aureus. The results are shown in Table II.

TABLE II GRAM POSITIVE MICROBIOLOGICAL ACTIVITY OF CLEANERS

	ACTIVE INGREDIENT	s. Aureus*	
10	FORMULA II - PINE OIL	0-/60	
	FORMULA IIIA - SORBIC ACID	0-/20	
	FORMULA IIIB - BENZOIC ACID	0-/20	

* Accomplished according to the ADAC-UDM procedure

Example III

A number of Examples of Formulation I of Example I were submitted to microbiological testing against staphylococcus aureus* (synthetic, nutrient), Salmonella choleraesuis* (synthetic nutrient), Pseudomonas aeruginosa* (nutrient) and Escherichia coli* (nutrient). The results are shown in Tables III and IV. It will be seen that these formulations have disinfectancy activity against both gram positive and gram negative organisms and thus broad spectrum disinfectancy:

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^{*} S. aureus -gram positive
S. choleraesuis -gram negative
P. aeruginosa -gram negative

TABLE III

GRAM POSITIVE MICROBIOLOGICAL ACTIVITY OF

PINE/OIL-SOLUBLE ACID BLENDS

•	ACTIVE INGREDIENTS	S. AUREUS*
15	Pine Oil + Sorbic Acid	59-/60
20	Pine Oil + Benzoic Acid	60-/60
·	Pine Oil + Phthallic Acid	59-/60
25	Pine Oil + Benzilic Acid	60-/60
	Pine Oil + Salicylic Acid	20-/20
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* Accomplished according to the AOAC-UDM procedure, which allows for one failure in a 50 tube test.

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TABLE IV

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BROAD SPECTRUM ANTIMICROBIAL ACTIVITY OF

A BENZOIC ACID/PINE OIL COMPOSITION

15	<u>ORGANISM</u>	MEDIA	RESULT*
20	S. aureus	synthetic	60-/60
	S. aureus	nutrient	59-/60
25	S. choleraesuis	synthetic	59-/60
	S. choleraesuis	nutrient	60-/60
30	P. aeruginosa	nutrient	60-/60
35	E. coli	nutrient	10-/10
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* Accomplished according to the AOAC-UDM procedure, which allows for one failure in a 60 tube test.

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It will be seen that the combination of pine oil and oil soluble organic acids has a clear, and surprising synergistic effect in providing disinfectancy activity against both gram positive and gram negative organisms and that a liquid cleaner is provided for hard surfaces having a broad spectrum activity.

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Claims

- 1. A liquid cleaner for hard surfaces having broad spectrum disinfectancy activity comprising pine oil and at least one oil soluble organic acid.
 - 2. The cleaner of Claim 1 wherein the composition has a pH of 0 to 6.
 - 3. The cleaner of Claim 1 which contains in addition organic detergent compounds.
 - 4. The cleaner of Claim 1 containing in addition isopropyl alcohol.

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- 5. The cleaner of Claim 1 containing in addition fenchyl alcohol.6. The cleaner of Claim 1 containing in addition ammonium hydroxide.7. The cleaner of Claim 1 containing in addition ethylene diamene tetra acetic acid.

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Re: European Patent Application No. 88 103 069.6

American Cyanamid Company Our Ref.: EA-6350

In the above-identified European patent application, please find enclosed a certified copy of U.S.A. patent application No. 07/028,814.

Further, it is requested that the following amendment on page I be made: in the last line, after "organic oil", the term "soluble acids such as, for example, benzoic acid" should be inserted. An accordingly amended replacement page I is enclosed in triplicate.

Respectfully submitted,

Günter Wächtershäuser Patent Attorney

Enclosures

Priority document

Replacement page 1, tripl.



Europäisches Patentamt European Patent Office Office européen des brevets

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Date of deferred publication of the search report: 05.09.90 Bulletin 90/36 7) Applicant: AMERICAN CYANAMID COMPANY 1937 West Main Street P.O. Box 60 Stamford Connecticut 06904-0060(US)

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Broad spectrum antimicrobial system for a hard surface cleaner.

(57) A liquid hard surface cleaner having broad spectrum disinfectancy activity based on a synergistic effect between pine oil and organic, oil soluble acids at a pH of 0 to 6. The cleaner has disinfectancy activity against both gram positive and gram negative organisms.

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EUROPEAN SEARCH REPORT

88 10 3069

		DERED TO BE RELEVAL	Relevant	CLASSIFICATION OF THE
ategory	Citation of document with in of relevant pas	ssages	to claim	APPLICATION (Int. Cl.4)
Α	FR-A- 342 747 (J.* Whole document *	-MA. DAVID)	1	C 11 D 3/48 C 11 D 3/18
Χ	DE-A- 254 129 (Dr * Whole document *	. K. RÜLKE)	1,3,5	C 11 D 3/20
X,L	CA-A-1 153 267 (AM * Page 1, line 2 - 3, line 26 - page 4 1-10; claims 1-6 *	ERICAN CYANAMID CO.) page 2, line 3; page , line 22; examples	1,3,4,7	·
A	DE-A-3 434 885 (PR * Abstract; claims line 1 - page 4, li 11-18; examples 5,6	1-5,13-17; page 3, ne 8; page 18, lines	1 ·	
X	US-A-3 703 472 (J. * Whole document *	F. SHAW et al.)	1,3,6,7	
X	DE-A-1 961 516 (NE * Page 1, line 9 - page 2, line 16 - p	page 6, from below; age 3, line 2; page	1-3	TECHNICAL FIELDS SEARCHED (Int. Cl.4)
	14 lines $2-17$ nage	8, line 18 - page 3, lines 7-19; page		C 11 D
		•		
	The present search report has I	been drawn up for all claims		
	Place of search	Date of completion of the search		Examiner
TH	IE HAGUE	21-06-1990	FIS	SCHER W.H.F.
X: p: Y: p:	CATEGORY OF CITED DOCUME articularly relevant if taken alone articularly relevant if combined with an ocument of the same category	E: earlier paten after the fill oother D: document ci	ted in the applicati ted for other reason	oblished on, or on os
O:0	echnological background on-written disclosure ntermediate document	& : member of t document	he same patent far	nily, corresponding